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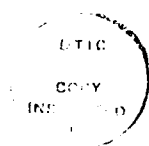
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Comparison of Single Point *Ab initio* Energies calculated using 3-21G and AM1 Geometries

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Single point *ab initio* calculations for a number of molecules, using various procedures with 3-21G or AM1 geometries, show that the AM1-based results seem to be better for high level *ab initio* procedures and for studies of reactions, as well as requiring less computing time.

Current *ab initio* methods usually give good estimates of heats of reaction if a large basis set is used and if allowance is made for electron correlation. *e.g.* by Moeller–Plesset (MP) perturbation theory. However. calculations of this kind require too much computing time to be carried out rigorously. *i.e.* with full geometry optimization, for any but small molecules. It has therefore become a standard practice[1] in such cases to calculate the geometries by a simple and correspondingly cheap method, usually the 3-21G model, and then to carry out single point calculations by the high level procedure. The same procedure is also commonly used in studies of the transition states (TS) of reactions where the cost of calculations by a correlated high level procedure is even more forbidding.

Use of this approach for systems where electron correlation plays a major role is clearly dubious because a simple RHF (spin-restricted Hartree–Fock) treatment is unlikely to give correct geometries in such cases, particularly if a small basis set is used. While this is necessarily the case for open shell systems, and also for the intermediates in many reactions, the same situation also exists for many 'normal' closed shell molecules, as Haddon *et al.*[2] have recently pointed out. Since there is no way to tell in advance whether or not this will be so in any given case, correlated procedures have to be used in all cases if the results obtained are to be reliable.

Extensive studies have shown that the normal (RHF) AM1[3] semi-empirical procedure gives good results in many cases

Table 1. Differences between energies calculated at the AM1 and 3-21G optimized geometries for neutral closed-shell species.[a]

	3-21G	6-31G				6-31G*			
Molecule	HF	HF	MP2	MP3	MP4	HF	MP2	MP3	MP4
H₂	1.78	1.47	1.84	2.03	2.13	—	—	—	—
H₂O	0.41	0.63	0.77	0.76	0.76	0.32	−0.78	−0.15	−0.14
CO₂	2.89	1.95	−5.08	−2.03	−4.37	5.52	−1.24	−1.40	−0.33
CO	2.54	2.28	−2.72	−0.21	−2.72	4.65	−0.17	2.16	0.26
NH₃	0.51	1.02	1.17	1.10	1.09	−1.00	−0.46	−0.48	−0.45
NH₃ (planar)	0.40	0.14	0.93	0.90	0.98	0.26	0.86	0.85	0.93
Methane	1.24	1.43	0.15	0.00	−0.29	1.30	0.66	0.55	0.36
Ethane	3.14	2.92	1.04	0.83	0.89	2.66	1.35	1.26	0.97
Ethene	1.25	1.06	−0.80	−0.88	−1.09	1.04	−0.13	−0.17	−0.38
Acetylene	0.21	−0.01	−1.04	−0.83	−0.98	0.11	−0.71	−0.51	−0.65
Propane	4.24	3.93	1.39	1.16	0.86	3.58	1.62	1.57	1.18
Propene	2.85	2.54	−0.08	−0.16	−0.44	2.50	0.40	0.64	0.32
Propyne	2.32	2.22	0.50	0.66	0.38	2.45	0.71	1.03	0.73
Cyclopropane	3.09	1.98	0.41	0.22	−0.02	2.46	0.65	0.57	0.26
Cyclopropene	2.84	1.44	0.13	0.67	−0.91	2.02	−0.36	0.04	−0.26
n-Butane	5.52	4.68	1.98	1.71	1.34	5.13	2.01	2.54	1.48
cis-buta-1,3-diene	2.78	2.43	−0.93	−0.85	−1.18	2.57	−0.15	0.08	−0.24
trans-buta-1,3-diene	2.27	1.90	−1.49	−1.43	−1.76	1.95	−0.56	−0.30	−0.70
Cyclobutene	2.58	1.74	−0.54	−0.41	−1.78	1.37	−0.72	−0.40	−0.68
Cyanoethane	4.11	3.46	−1.61	−0.31	−1.32	4.30	−0.37	0.90	0.01
Cyanoethene	2.30	1.56	−3.63	−2.16	−3.14	2.55	−1.99	−0.66	−1.43
cis-Dicyanoethene	3.33	1.96	−6.96	−3.71	−5.59	3.92	−4.15	−1.92	−2.80
Nitromethane	5.97	3.09	9.61	6.25	7.78	−1.81	4.75	1.90	−4.88
N,N-Dimethylamine	4.17	4.04	1.97	1.67	1.45	2.42	0.92	0.88	0.58
Dimethyl ether	3.75	3.71	1.51	1.16	0.98	2.26	0.75	0.63	0.38
Acetaldehyde	2.45	2.06	−1.20	−0.73	−1.32	3.30	0.35	0.87	0.33
Acetone	3.56	3.14	−0.70	−0.28	−0.88	4.39	1.22	1.69	1.07
trans-propen-3-ol	2.58	2.58	−0.16	−0.12	−0.36	1.52	−0.43	−0.31	−0.54
cis-propen-3-ol	2.04	1.07	−0.46	−0.41	−0.64	1.93	−0.60	−0.48	−0.60
Cyclopentadiene	3.03	2.31	−1.93	−1.52	−1.89	2.64	−0.82	−0.21	−0.60
Benzene	2.40	1.93	−2.50	0.78	−2.74	1.78	−0.79	−0.58	−0.97
Average	2.66	2.15	−0.27	0.11	−0.47	2.24	0.06	0.35	−0.23
Std. dev.	1.36	1.11	2.74	1.69	2.32	1.67	1.48	1.03	1.23

[a] (kcal mol⁻¹); all 3-21G geometries are from R. A. Whiteside, M. J. Frisch, and J. A. Pople, 'The Carnegie-Mellon Quantum Chemistry Archive,' 3rd edn., Carnegie-Mellon University, Pittsburgh, 1983; AM1 optimizations performed starting at 3-21G geometries and using identical symmetry constraints; a negative result indicates that the AM1 geometry is lower in energy at that single point than the 3-21G geometry.

Table 2. Differences between energies calculated at the AM1 and the UHF/3-21G optimized geometries for neutral radicals.[a]

	3-21G	6-31G				6-31G*			
Molecule	HF	HF	MP2	MP3	MP4	HF	MP2	MP3	MP4
NO·	2.85	1.50	−12.46	−7.62	−4.57	−5.23	−13.28	−10.15	−6.88
HCO·	2.87	3.00	3.79	3.47	3.38	4.91	5.96	4.80	4.64
CH₃·	0.26	0.26	−0.17	−0.26	−0.31	0.23	−0.01	−0.07	−0.13
C₂H₅·	2.51	2.36	1.26	1.15	1.03	2.22	1.10	1.09	0.93
C₂H₃·	8.16	8.55	6.04	5.95	5.86	8.73	4.81	4.92	5.00

[a] (kcal mol⁻¹); all 3-21G geometries are from R. A. Whiteside, M. J. Frisch, and J. A. Pople, 'The Carnegie-Mellon Quantum Chemistry Archive,' 3rd edn., Carnegie-Mellon University, Pittsburgh, 1983; AM1 optimizations performed using RHF half-electron approximation and starting at 3-21G geometries using identical symmetry constraints; a negative result indicates that the AM1 geometry is lower in energy at that single point than the 3-21G.

where allowance for correlation has to be made in *ab initio* calculations. Indeed, the same is true even in the case of reactions,[4] provided that the intermediates are not biradicals or closely related to biradicals.[5] AM1, like our earlier semi-empirical procedures (MINDO/3[6] and MNDO[7]), allows for electron correlation *via* the parametrization. This built-in compensation fails only in cases where the correlation between two or more electrons becomes extreme.

It therefore occurred to us that AM1 geometries might provide a better basis for single point calculations by high level correlated *ab initio* procedures than the simple RHF *ab initio* geometries that have hitherto been used in this connection. Such an approach would also save computing time because AM1 geometry optimizations are faster by three orders of magnitude than those using the 3-21G model. We have now tested this suggestion by carrying out parallel single point

Table 3. Results for the cyclobutane to cis-buta-1,3-diene reaction.[a]

Method	ΔH_{rxn}	ΔH_{act}
Experimental[b]	−9.1	32.9
Ab initio[c]	−6.2	42.4
AM1[d]	−15.1	36.0
HF/3-21G//AM1	−14.4	41.2
HF/6-31G//AM1	−15.9	46.7
MP2/6-31G//AM1	−13.9	32.2
MP3/6-31G//AM1	−13.5	34.8
MP4/6-31G//AM1	−14.9	33.9
HF/6-31G*//AM1	−8.3	42.2
MP2/6-31G*//AM1	−4.0	37.5
MP3/6-31G*//AM1	−5.1	40.4
MP4/6-31G*//AM1	−6.1	39.9

[a] (kcal mol^{-1}). [b] Ref. 8. [c] Ref. 9 (TCSCF + CISD DZ + d, Huzinaga-Dunning). [d] Ref. 3.

calculations by various *ab initio* procedures, using AM1 and 3-21G geometries.

Further work is clearly needed to assess the general value of AM1 as an aid in *ab initio* calculations, in particular in studies of reactions. It is to be hoped that those in the *ab initio* area will make such information available. The additional cost of an AM1 geometry optimization, and a single point *ab initio* calculation using AM1 geometry, is trivial in relation to the cost of a complete *ab initio* study.

Table 1 shows the results for 31 neutral closed-shell molecules and Table 2 those for 5 neutral radicals. Each table lists the difference between the total energies calculated at the AM1 geometry, and at the 3-21G geometry, for each molecule at various levels. A negative result indicates that the single point calculation at the AM1 geometry yielded a lower energy than that at the 3-21G geometry. Since the latter is necessarily more positive than the energy calculated with full geometry optimization by the relevant higher level *ab initio* procedure, a negative difference indicates that the single point calculation at the AM1 geometry gave a better estimate than a corresponding calculation using the 3-21G geometry.

The results in Tables 1 and 2 are noteworthy in that they show the much more rapid AM1 procedure to be at least on a par with, if not better than, the 3-21G *ab initio* model. This is especially true for correlated calculations at the 6-31G* level. For the 31 closed-shell neutral species studied, the MP4/6-31G* energy at the AM1 geometry is lower by an average of 0.23 kcal mol^{-1} than that at the 3-21G geometry (cal = 4.184 J).

The advantage of AM1 should become more pronounced in situations where changes in correlation play a role, in particular in calculating enthalpies of activation for reactions where the transition states are not biradicals. Table 3 summarizes results for the conrotary opening of cyclobutene to cis-1,3-butadiene. While the single point calculations at the AM1 geometry vary considerably with the procedure used, all but one of them lead to an activation energy closer to the experiment[8] than that given by a detailed high level *ab initio* study.[9] It is interesting to note that AM1 itself also led to a better estimate.

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